

Spatial Variation in the Accumulation of Elements in Thalli of the Lichen *Pseudevernia furfuracea* (L.) Zopf Transplanted Around a Biomass Power Plant in Italy

Lucio Lucadamo¹ · Anna Corapi¹ · Stefano Loppi² · Rosanna De Rosa¹ · Donatella Barca¹ · Giovanni Vespasiano¹ · Luana Gallo¹

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Abstract Thalli of the lichen *Pseudevernia furfuracea* were transplanted for 3 months at 32 sites located in and around an industrial area of S Italy whose main anthropogenic sources of atmospheric trace elements are a biomass power plant and vehicular emissions. Meteorological stations were deployed at four sites for finer detection of local wind patterns. The station near the biomass power plant showed a significant S-SE wind component not detectable by measurements made at the regional scale or by the other local meteorological stations. Sb, Sn, and Mo showed a very high degree of covariance and a statistically significant correlation with traffic rate. No element concentrations in the exposed thalli were correlated with distance from the biomass power plant, although Ti and Co

concentrations showed a significant correlation with the “Potential Number of Times the Winds coming from the biomass power plant Reach each exposure Site” (PNTWRS). This value is calculated dividing the time (minutes) during the experimental trimester that the wind blows from the power plant into each of the four geographical sides by the time (minutes) the winds passing through the power plant take to reach the exposure sites in each of the four geographical sides.) during the period of thalli transplantation. Moreover, there were significant differences among clusters of sites with different levels of enrichment of Ti, Co, Al, V, and Cu and a “local control” group. These results, together with the high covariance of the Al–Ti and V–Co pairs, indicate an association between the biomass power plant and spatial variation of Ti, Co, Al, and V levels in the transplanted lichens. The nature of the fuels used in the biomass power plant explains the spatial variation of As, Cr, Cu, and Zn concentrations.

✉ Lucio Lucadamo
lucio.lucadamo@unical.it

Anna Corapi
annacorapi@libero.it

Stefano Loppi
stefano.loppi@unisi.it

Rosanna De Rosa
rosanna.derosa@unical.it

Donatella Barca
d.barca@unical.it

Giovanni Vespasiano
giovanni.vespasiano@unical.it

Luana Gallo
luana.gallo@unical.it

¹ DiBEST (Dipartimento di Biologia, Ecologia e Scienze della Terra), Università della Calabria, 87036 Arcavacata di Rende (CS), Italy

² Dipartimento di Scienze della Vita, Università di Siena, 53100 Siena, Italy

Lichens are considered the most effective organisms for biomonitoring of air pollution. Because they colonize virtually all types of terrestrial environments, they can be widely used as bioindicators of phytotoxic air pollutants and as bioaccumulators of persistent air contaminants (Nimis et al. 2002). Because of their ability to accumulate amounts of elements vastly exceeding their nutritional requirements (Backor and Loppi 2009), in situ lichen species can profitably be used to monitor pollution phenomena, especially long-term ones (Loppi and De Dominicis 1996; Loppi et al. 1998; Paoli et al. 2012). However, when the pollution levels exceed their homeostatic capacities and drastically reduce the local flora, bioaccumulation studies are still feasible by means of the transplantation technique (Mikhailova 2002), which has the

advantage of allowing a wide variety of experimental designs particularly suited to the detection of spatial contamination patterns.

Nonetheless, even well-planned transplantation monitoring programs can fail to detect spatial contamination trends without an adequate evaluation of local wind patterns and when differences (geo-pedological and meso-climatic) between as well the lichen source area as a control group of stations outside the monitoring area (and far enough to avoid autocorrelation) and the lichen exposure area hinder a careful evaluation of the contribution of local sources to atmospheric contamination processes.

The main goal of the present study was to determine the spatial patterns of element accumulation in thalli of the lichen *Pseudevernia furfuracea* (L.) Zopf transplanted in and around an industrial area of S Italy where the major contributors to atmospheric element enrichment are a biomass power plant (the other buildings in the area are mostly houses and offices of tertiary service firms) and traffic. In particular we: (1) determined the covariance as well between element concentrations in exposed thalli as between distance of each station from biomass power plant and element concentrations in transplants, (2) measured both the local wind frequencies, directions and velocities (for calculating element spatial dispersion parameters) and the traffic rate of the local road network to search for association between the spatial distribution of elements within the study area and their local anthropogenic sources, (3) identified a “local control” group to assess more accurately the contribution of anthropogenic sources to the atmospheric enrichment of elements and to test for statistically significant differences between it and clusters of sites with different element concentrations in the exposed thalli.

Materials and Methods

Study Area

The study area (Calabria Region, S Italy) extends more than ca. 27 km². It is entirely crossed from N to S by the A3 motorway and includes state highways 19 and 19bis, the northern part of the town of Rende (ca. 35,000 inhabitants) and a biomass power plant (nominal electrical power 13.3 MW) in the central part fueled by wood from manufacturing wastes and thinning of the Sila forests and by expired olive pomace. The elevation range is 100–300 m a.s.l. Prevailing winds blow from WNW. The annual values of climatic parameters are rainfall 1237 mm,

mean temperature 16.4 °C and mean relative humidity (RH) 65.1 % (ARPACAL 2014).

Lichen Transplantation

Because lichen colonization in the study area was not sufficient to perform atmospheric monitoring with in situ populations, the transplantation technique was preferred. Thalli of the lichen *Pseudevernia furfuracea* (L.) Zopf, collected together with their supporting substrate (tree twigs) at a remote site (La Fossiatà) at approximately 1600 m a.s.l. in the Sila plateau, were transplanted in the study area at 32 experimental sites (Fig. 1). The annual values of climatic parameters in the source area (SA) are rainfall 1644 mm, mean temperature 10.1 °C and mean RH 76.8 %.

At each transplantation site, three twigs bearing the lichens were attached to tree branches or poles with plastic strings at a height of ca. 3 m above ground to avoid vandalism and minimize any geogenic contribution to element trapping by the lichens. The final site density was 1.2 per km², a quite high value compared with similar studies (Ljubic Mlakar et al. 2011; Sujetoviene 2013; Jeran et al. 1995). Thalli were exposed for three months, from February 20, 2013 to May 20, 2013.

Local Wind Monitoring

Four meteorological stations (Vantage Vue—Davis) were deployed to monitor wind speed and direction at four of the 32 sampling sites, one for each geographical side of the study area. One meteorological station was located as close as possible to the biomass power plant (at site 13, where the monitoring unit could be set up without danger of damage or theft) to obtain a good estimate of the wind conditions experienced by that part of the study area. We consider the data of station 13 a realistic estimate of wind conditions at biomass plant site due to: (a) the relatively modest distance, (b) the lack of any relief surrounding the two sites with a flat territory dividing them, and (c) the extremely reduced altitudinal gradient between these stations (1.9 cm/m) (Denison et al. 2001; MEASNET 2009).

The stations were provided with a Weather Link data logger whose frequency of storing the measured parameters was set at once per 15 min for a total of 96 values memorized for each parameter every 24 h. The data were transferred biweekly to spreadsheets for further analysis. Each station was set at the top of a 2.5-m high steel rod held in place by a concrete base and located as far as possible (at least ten times the height of the nearby building) from any obstacle that might change wind direction at ground level (AASC 1985; EPA 1987).

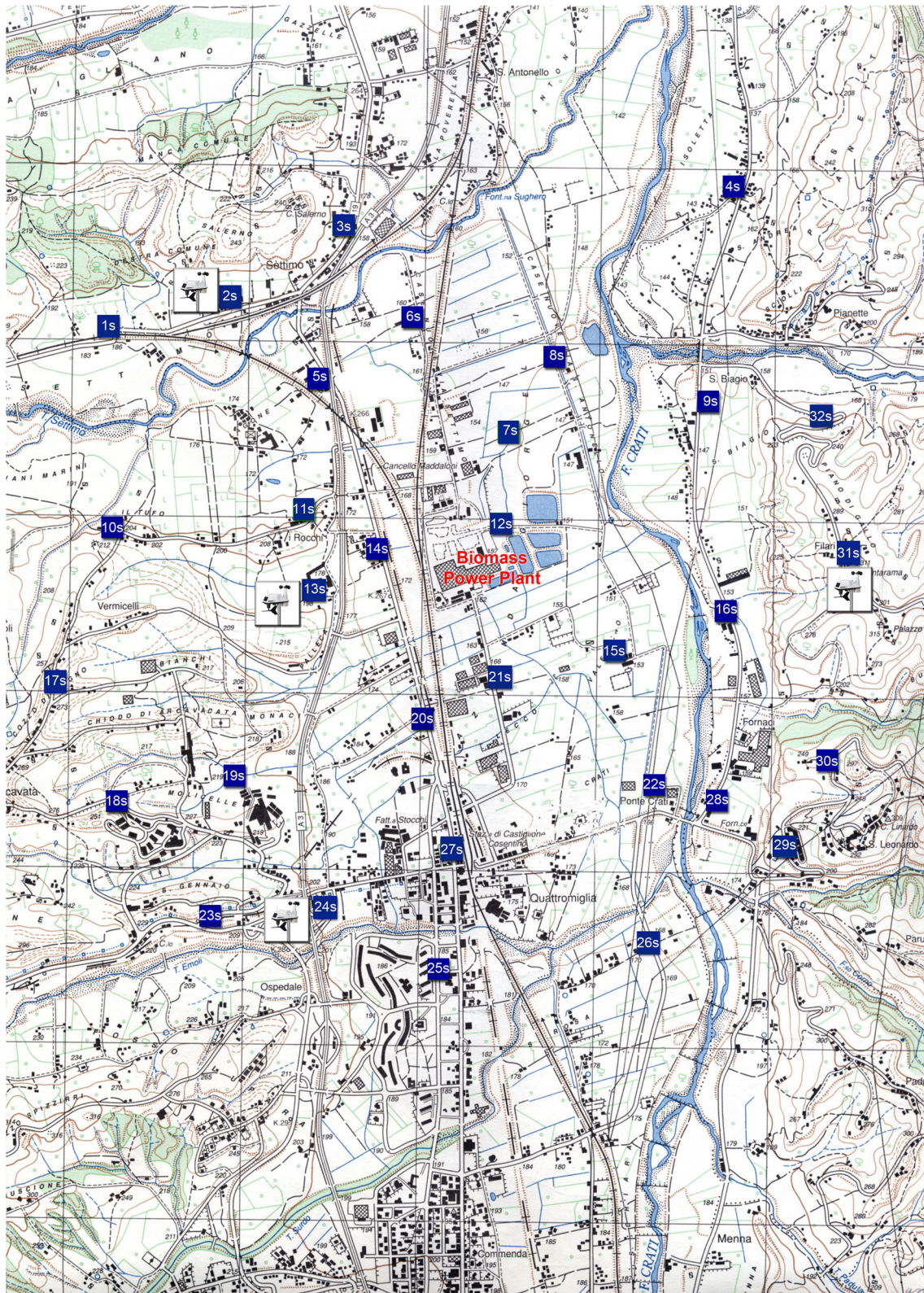


Fig. 1 Study area and location of the 32 exposure sites, including those where the meteorological stations were set up

Elemental Analysis

At the end of the exposure period, the lichen samples were retrieved, transported to the laboratory, and air-dried to constant weight. The samples were not rinsed to avoid losing particles trapped on the lichen surface. Three subsamples (1 for each of the 3 whole thalli exposed at the 32 sites) were used to measure the element concentrations at the end of the exposure period while five subsamples (each from a different thallus) were analyzed from the source area before the transplantation. The subsamples were mixed and immersed in liquid nitrogen until brittle and then pulverized and homogenized with a ceramic mortar and pestle. Aliquots of 100 mg were weighed, transferred to Teflon vials, and mineralized with 12 mL of ultrapure HNO₃ for 30 min in a microwave oven (Milestone Ethos 900). The certified reference material BCR 482 “Lichen *Pseudevernia furfuracea* (L.) Zopf” was used for the evaluation of accuracy and precision. Element concentrations were measured by ICP-MS (Elan DRC Perkin-Elmer SCIEX) at the Laboratory of Mass Spectrometry of the Department of Biology, Ecology, and Earth Sciences (University of Calabria) and expressed on a dry weight basis. The analyzed elements (Al, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn) were selected because of their representation in the atmospheric emissions from the main anthropogenic sources of the study area (Eastern Research Group 2001; Demirbas 2003).

Statistical Analyses

To detect similar spatial patterns of element concentrations within the study area, we converted the original data to ranks and then calculated a nonparametric (Spearman) correlation coefficient and classified the element concentration ranks versus exposure sites dataset using the Euclidean distance as dissimilarity measure and the minimum variance method of Ward as clustering criterion. Conversion of the original data into ranks was performed to avoid the bias of segregating macroelements from trace elements as a consequence of their natural abundance/occurrence.

Associations between the main local anthropogenic sources of atmospheric contamination (traffic and biomass power plant) and element concentrations in the exposed thalli were evaluated by means of three nonparametric correlation analyses: (a) lichen element concentration—intensity of traffic (vehicle/h) at each site (the latter parameter was measured by counting the number of vehicles passing during the same time interval (9 a.m.–2 p.m.)), (b) lichen element concentration at each site—distance between exposure sites and biomass power plant, (c) lichen element concentration at each site—Potential Number of

Times the Winds coming from the biomass power plant Reach each exposure Site (PNTWRS). The latter parameter was calculated, because the dispersion of the biomass power plant emissions over the study area depends strongly on wind speed and direction. Thus, we calculated the time (Minutes) that the Winds passing through the power plant (a value assigned using site 13 data) take to Reach the exposure Sites (MWRS) in each of the four geographical sides on the basis of distances from the power plant of exposure sites located on the geographical sides and the directions and speeds of winds coming from each of the four geographical sides and passing through the power plant location. The input frequency into a geographical side of the winds passing through the power plant was assumed to be the same as the provenance frequency from the opposite geographical side (the value measured by meteorological stations) and it was used to calculate the time (minutes) during the experimental trimester that the wind blows from the power plant into each of the four geographical sides. This value was divided by MWRS to calculate the potential number of times the winds coming from the power plant reach each exposure site (PNTWRS).

Non-metric Multidimensional Scaling (NMS) was applied to the element concentrations versus exposure sites dataset with a two-axes final solution (McCune and Grace 2002) to detect clusters of sites showing a high level of similarity in element concentrations. The multi-response permutation procedure (MRPP) was performed with the Sorensen index as a measure of similarity to test the null hypothesis of no differences among the clusters detected by NMS. One-way ANOVA with a post-hoc multiple comparison (Tukey test) was run to test the null hypothesis of no differences in the concentrations of each element in the clusters revealed by the ordination techniques. The statistical analyses were performed with the software packages Minitab Release 13.2 and PC-ORD 4. We created isoconcentration maps with GIS software, adopting suitable semivariogram models to describe the spatial dependence of each variable of interest and ordinary Kriging as interpolation method.

Results

The accuracy and precision of the analyses were checked by determinations (seven replicates) of the certified reference material BCR-482 (Lichen *Pseudevernia furfuracea*). The accuracy was 4 % and the precision 3 %. Table 1 shows the percentage distribution of the 32 exposure sites ranked into different classes of atmospheric element enrichment based on the comparison with environmental quality standards and scales of naturality/contamination (Bargagli and Nimis 2002; Rhoades 1999; Corapi 2011).

Table 1 Percentage distribution of the 32 exposure sites in different classes of atmospheric element enrichment based on the comparison of the experimentally measured element concentrations with scales of naturality/contamination and environmental quality standards (see text for references)

Element	No enrichment	Slight	Moderate	High	Very high
Al	0	34	66	0	0
Mn	0	38	59	3	0
Ti	0	16	84	0	0
Sn	53	47	0	0	0
Sb	3	66	22	9	0
V	13	84	3	0	0
Cr	78	13	3	3	3
Co	0	100	0	0	0
Ni	100	0	0	0	0
Cu	69	0	9	19	3
Mo	75	25	0	0	0
Pb	100	0	0	0	0
Zn	69	7	9	9	6
As	84	0	3	0	13
Cd	100	0	0	0	0

The vast majority of sites showed moderate enrichment for Al, Mn, and Ti and slight enrichment for Sb, V, and Co, whereas Cr, Cu, Zn, and As showed no enrichment except at some of the sites where they approached high or very high values. Lastly, Ni, Pb, and Cd always showed no atmospheric enrichment. Due to the low levels of Ni, Pb, and Cd in the exposed thalli, these elements were excluded from the subsequent statistical analyses.

Figure 2 shows the results of cluster analysis of the element concentration ranks versus exposure sites dataset. Three main clusters can be distinguished: the first included Sn, Mo, and Sb with the highest similarity between

elements; the second included Al, Ti, V, and Co with an intermediate level of similarity; and the third included Cr, Cu, As, and Zn with a low level of similarity. Manganese showed the lowest similarity with all the other elements.

The results of the Spearman correlation analysis of element concentration ranks are reported in Table 2. They are consistent with the output of the cluster analysis: the element pairs with the highest *r* values are Sn–Mo, Sn–Sb, Sb–Mo, Al–Ti, and V–Co, whereas As, Cu, Cr, and Zn showed only moderate correlations and Mn did not show any significant correlation.

There were significant correlations between the spatial variation of traffic intensity (vehicles/h) and the Sb, Sn, Mo, and Cu concentrations in transplanted lichens (Sb: *r* = 0.56, *p* < 0.01; Sn: *r* = 0.66, *p* < 0.0005; Mo: *r* = 0.62, *p* < 0.0005; Cu: *r* = 0.38, *p* < 0.05).

The nonparametric correlation analysis of element concentrations in exposed thalli and the distance between the exposure sites and the biomass power plant did not reveal any significant association (*p* > 0.05).

Table 3 shows the distance of the sites in each of the four geographical sides from the power plant and the calculated values of MWRS and PNTWRS. The only elements whose concentration in exposed thalli showed a significant correlation with PNTWRS were Ti (*r* = 0.38, *p* < 0.05) and Co (*r* = 0.36, *p* < 0.05)

Table 4 shows the percentage distribution of wind direction monitored at sites 13, 31, 2, and 24. The most frequent average wind directions were from SW (36 %) and NW (28.5 %). Interestingly, at site 13 the meteorological station revealed not only the most frequent wind blowing from the SE sector (30 %) but also the strongest gusts of wind with the highest speed (Fig. 3) during the entire monitoring period (average difference between site 13 and the others: February +66 %; March +38 %; April +41 %; May +43 %). The highest wind speeds were in

Fig. 2 Dendrogram resulting from the cluster analysis of the element concentration ranks versus exposure sites database

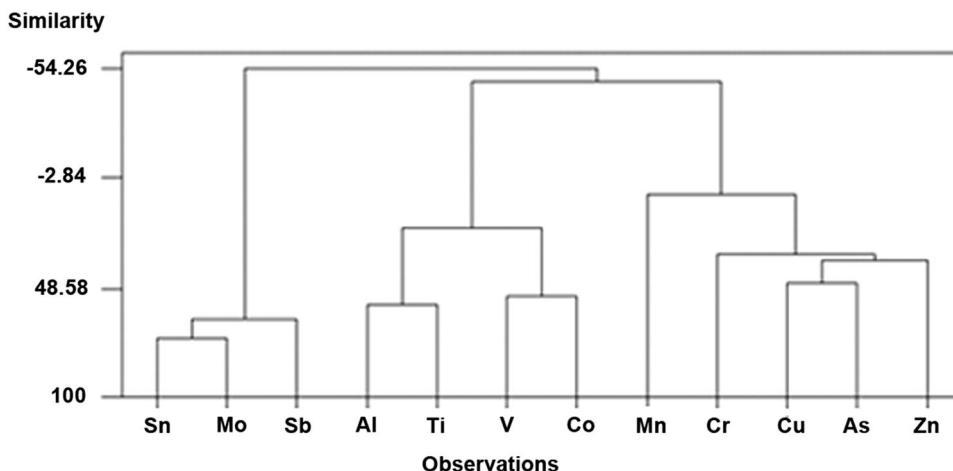


Table 2 Coefficients of determination (r^2) of all the associations between pairs of elements showing a value of $p < 0.05$

Correlation	r^2	Correlation	r^2
Sn–Mo	0.83	Ti–V	0.22
Sn–Sb	0.79	Co–Cu	0.22
Sb–Mo	0.69	Ti–Co	0.20
Al–Ti	0.61	Sb–Zn	0.20
V–Co	0.55	Cr–Cu	0.20
Cu–As	0.45	Co–Mo	0.20
Al–V	0.42	Sn–Co	0.19
Al–Co	0.37	Sb–Cr	0.19
Co–Cr	0.35	V–Mo	0.15
Cr–As	0.35	Co–As	0.15
Mo–Cu	0.35	Sb–V	0.14
Cu–Zn	0.34	Al–Cr	0.14
Sb–Cu	0.31	Sn–V	0.14
Zn–As	0.28	Co–Zn	0.14
Sb–Co	0.27	Sn–Zn	0.12
Sn–Cu	0.26	V–Cr	0.12
Cr–Zn	0.26		

March and the lowest between the end of April and the beginning of May at all four sites.

Figure 4 shows the ordination diagram that emerged from the results of NMS applied to the element concentrations versus exposure sites dataset. The two-axes solution explained 72 % of total variation, of which 56 % was associated with axis 1 and 16 % with axis 2. Final stress and instability were respectively 8.9 and 0.0005, suggesting a good ordination result. Most sites are arranged along axis 1 where five clusters can be distinguished. The results of the MRPP to test the null hypothesis of no difference among the five clusters [$T = -11.1$, $p < 0.001$; A (Chance-corrected within cluster agreement) = 0.37] allowed us to reject with extremely high probability a stochastic origin of their formation, supporting an alternative (deterministic) explanation.

The concentrations of the 12 elements in the five clusters, the mean of the clusters, and the coefficient of variation are reported in Table 5, along with the mean concentrations measured in thalli from the source area before exposure. Most elements showed a low coefficient of variation, except for Cr, Cu, Zn, and As whose high value is clearly ascribable to outliers measured at some sites. Table 6 shows the results of one-way ANOVA and post-hoc multiple comparison (Tukey test) run to test the null hypothesis of no differences in element concentrations among the five clusters that emerged from NMS. Cluster C1 always showed the lowest mean concentration for all elements, whereas clusters C4 and C5 showed the highest mean concentrations for Al, Ti, V, Co, Cu, and Mo; all of

them except Mo differed significantly from the other clusters (C1, C2, and C3). Figures 5, 6, 7, 8 show the isoconcentration maps of the spatial distributions of Al, Ti, V, and Co. The highest values were in the NE and NW sectors where most of the sites of clusters 4 and 5 are located.

Discussion

Among the analyzed elements, Sn, Sb, and Mo showed the highest covariance (as indicated by cluster analysis and nonparametric correlation), strongly supporting the hypothesis of a common local anthropogenic source. We consider this source to be vehicular traffic, as supported by the positive correlation between the concentrations of these three elements in exposed thalli and the traffic rate. The lower association of Cu with both traffic intensity and Sn, Sb, and Mo concentrations suggests that the contribution of traffic to Cu atmospheric enrichment is not as strong as it is to that of the other three elements. The emission of these elements by traffic (Schauer et al. 2006) is usually low (Sn = 0.006 mg/km, Mo = 0.009 mg/km, Sb = 0.013 mg/km), but the total exhaust also depends on the traffic rate. Approximately 25 % of the vehicle flow measurements made in our study area were comparable with those performed in some of the main Italian motorways or urban areas (Perrino et al. 2003).

Interestingly, Sb, Sn, and Mo are specific tracers of car mechanical consumption (Schauer et al. 2006). The southern part of the study area contains the town of Rende, which showed the highest traffic rates (site 24 = 1594 vehicles/h, site 27 = 1455 vehicles/h, site 20 = 1401 vehicles/h) and has a large number of crossroads, roundabouts, and traffic lights, resulting in marked stress on brakes and tires (Bukowiecki et al. 2009). Nevertheless, many studies (Ayodele and Oluyomi 2011; Amusan et al. 2003; Xuedong et al. 2013) have shown that particulate vehicle emissions quickly abate within tens of meters from the roads where they are generated (due to the near ground source), so that their effect on long-range (kilometers) contamination processes is modest and thus they are effective tracers of road networks and related vehicle flows.

The variation of Ti and Co concentrations in transplanted lichens in the four geographical sides of the study area (NE, NW, SE, SW) were significantly associated with the potential number of times the winds coming from the biomass power plant reach each exposure site (PNTWRS). Although this association was moderate, it must be considered relevant because the local wind speeds and directions are strongly affected by topography and temperature variation (Chock et al. 2005; Stull 1988; Whiteman 1990) and despite the effect of these confounding factors the association could still be detected.

Table 3 Distance of the exposure sites from the biomass power plant and calculated values of MWRS and PNTWRS

Geographical sides where the exposure sites are located	Exposure sites	Distance of exposure sites from the biomass power plant (km)	(MWRS) Time (min) the winds passing through the power plant take to reach each exposure site	(PNTWRS) potential number of times the winds coming from the power plant reach each exposure site during the 3-month exposure period
NW	1	3.56	22'36"	1723
NW	2	2.97	18'53"	2063
NW	3	2.99	19'00"	2050
NW	5	2.06	13'07"	2972
NW	6	2.10	13'30"	2918
NW	10	2.94	18'38"	2090
NW	11	1.40	8'54"	4377
NW	13	1.25	7'56"	4908
NW	14	0.76	4'49"	8098
NE	4	3.84	21'16"	2021
NE	7	1.17	6'29"	6616
NE	9	2.41	13'18"	3230
NE	8	1.88	10'22"	4143
NE	12	0.51	2'50"	15192
NE	32	3.18	17'36"	2441
NE	31	3.18	17'36"	2441
SW	17	3.56	26'47"	785
SW	18	3.47	26'04"	807
SW	19	2.59	19'32"	1077
SW	20	1.31	9'50"	2140
SW	23	3.58	26'55"	781
SW	24	3.05	22'56"	917
SW	25	3.35	25'13"	834
SW	27	2.33	17'31"	1200
SE	15	1.40	8'32"	3123
SE	16	2.14	13'2"	2045
SE	21	0.95	5'46"	4622
SE	22	2.39	14'32"	1834
SE	26	3.47	21'07"	1263
SE	28	2.84	17'18"	1541
SE	29	3.50	21'20"	1249
SE	30	3.41	20'46"	1284

Table 4 Frequency distribution of wind (provenance) directions measured by meteorological stations at the four exposure sites

Sites	SW	SE	NW	NE
13	33	30	21	16
31	43	16	25	16
2	26	21	40	13
24	42	12	29	17
Average	36	20	29	16

Spatial variations of Ti and Co were correlated strongly with Al and V concentrations in lichen transplants, respectively, even though the latter two elements did not

covariate with PNTWRS. The lack of association for aluminum may be due to the geogenic contribution to atmospheric particulate that affects the Al content in exposed thalli, whereas V, although mainly emitted by anthropogenic sources (Visschedijk et al. 2013), was the element with the highest number of slight enrichments (Table 1).

Ti, Co, Al, and V are all found in raw materials, fuels and atmospheric emissions associated with biomass power plants (Thy et al. 2008; Sippula et al. 2007; Rector et al. 2013). Moreover, coniferous trees, which dominate the Sila forests and provide fuel for the biomass power plant, are rich in aluminum (CEN/TC 2003).

Fig. 3 Wind speeds measured at the exposure sites with meteorological stations (on the abscissa: number of days the meteorological parameters were measured)

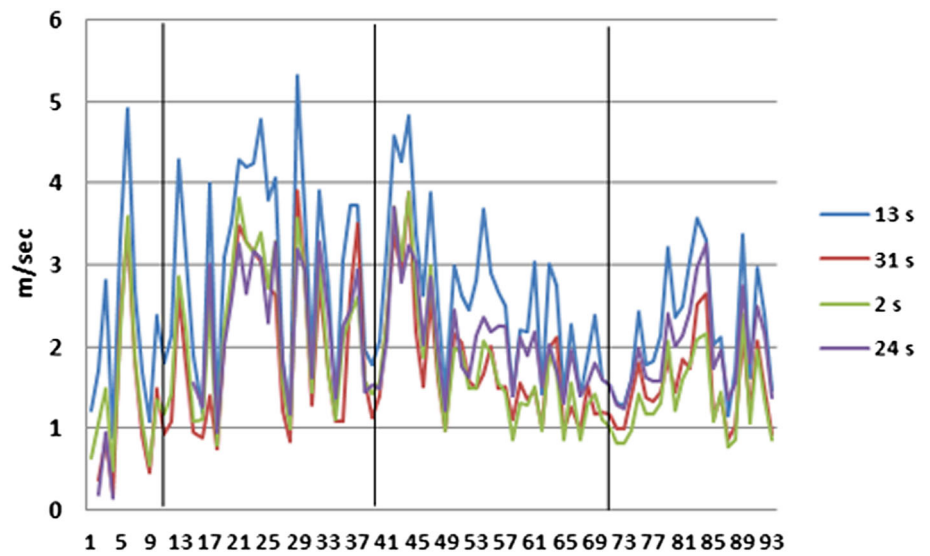


Fig. 4 Diagram resulting from NMS applied to the element concentrations versus exposure sites database

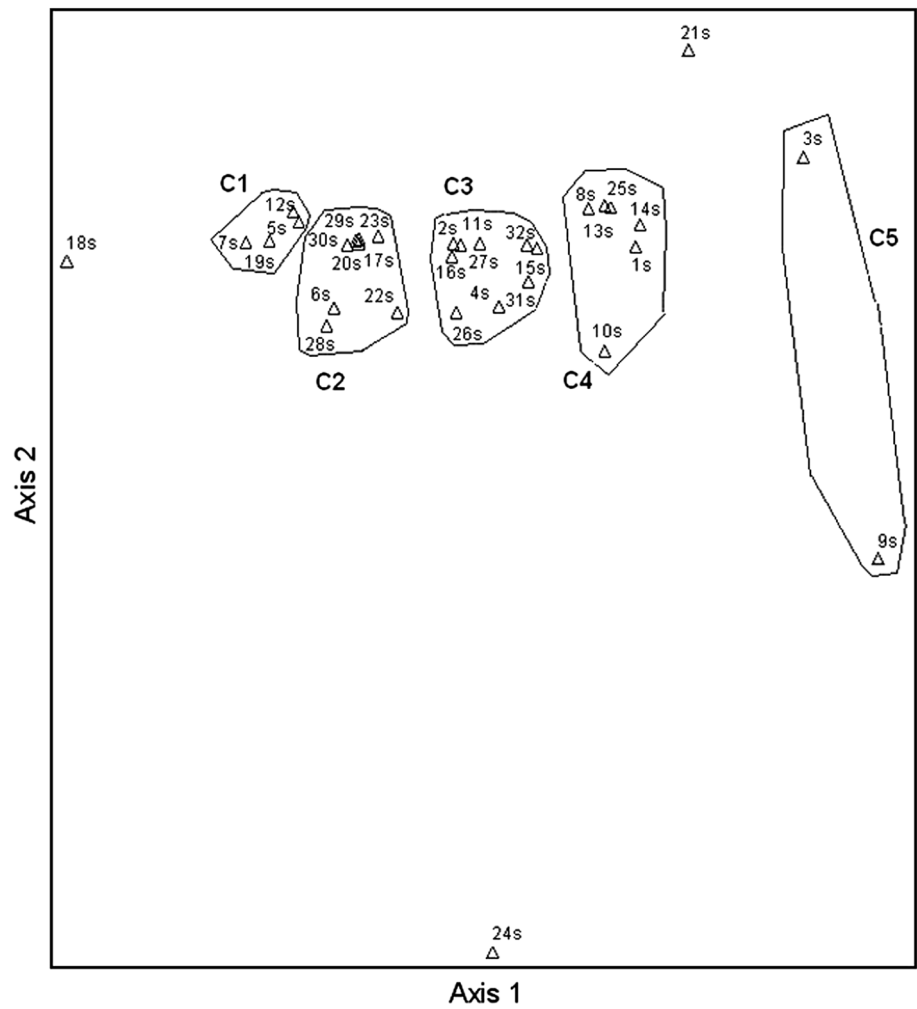


Table 5 Element concentrations ($\mu\text{g g}^{-1}$ d.w.) in the five clusters, mean of the clusters, coefficient of variation, and mean concentrations ($n = 5$) of the same elements measured in the source area

Sites	Clusters	Al	Mn	Ti	Sn	Sb	V	Cr	Co	Cu	Mo	Zn	As
5	C1	1468	57	70	0.38	0.18	2.98	2.29	0.45	5.78	0.19	32	0.31
7		1401	53	53	0.64	0.34	3.93	2.71	0.66	8.84	0.31	78	0.34
12		1431	71	92	0.31	0.20	3.49	3.36	0.49	5.74	0.19	33	0.28
18		1130	53	37	0.23	0.09	2.62	3.09	0.41	5.77	0.18	62	1.00
19		1448	60	38	0.52	0.25	3.35	2.79	0.52	7.52	0.24	79	0.30
	Mean	1376	59	58	0.42	0.21	3.27	2.85	0.51	6.73	0.22	57	0.45
	CV (%)	10	13	40	39	43	15	14	19	21	25	41	70
6	C2	1553	82	94	0.31	0.14	3.45	9.51	0.58	26.79	0.16	118	32
17		1603	71	111	0.34	0.13	3.42	2.46	0.50	5.36	0.19	30	0.20
20		1545	74	88	1.09	0.53	3.17	3.10	0.56	11.55	0.39	39	0.40
22		1640	58	109	0.86	0.47	3.70	3.16	0.54	36.06	0.35	138	0.30
23		1576	62	84	0.72	0.40	3.58	3.05	0.53	9.02	0.28	39	0.29
28		1555	68	85	0.82	0.61	3.05	25.6	0.54	63.74	0.35	65	63
29		1566	74	86	0.41	0.19	3.61	2.83	0.50	6.38	0.21	33	0.41
30		1582	56	78	0.32	0.13	3.18	2.51	0.47	5.47	0.21	30	0.30
	Mean	1578	68	92	0.61	0.32	3.40	6.53	0.53	21	0.27	62	12
	CV (%)	2	13	13	49	62	7	123	7	101	32	695	193
2	C3	1769	72	99	0.31	0.12	3.33	2.69	0.49	4.82	0.17	35	0.25
4		1822	54	93	0.40	0.19	3.78	2.79	0.54	116.81	0.28	37	0.56
11		1784	50	106	0.32	0.18	3.35	2.80	0.51	5.82	0.25	31	0.22
15		1932	56	132	0.53	0.27	3.51	3.18	0.54	6.78	0.28	47	0.31
16		1752	78	100	0.61	0.32	3.73	3.01	0.61	33.85	0.27	36	0.32
24		1719	64	97	1.08	0.46	3.60	3.24	0.56	11.08	0.37	2707	0.39
26		1780	63	54	1.01	1.23	4.16	5.31	0.71	18.51	0.39	115	7.98
27		1832	50	90	0.54	0.28	3.87	3.09	0.51	7.93	0.27	31	0.31
31		1905	73	96	0.31	0.17	3.97	5.19	0.59	9.31	0.18	142	2.06
32		1945	73	89	0.30	0.11	4.07	3.15	0.62	5.56	0.18	29	0.38
	Mean	1824	63	96	0.54	0.33	3.74	3.45	0.57	22.05	0.26	321	1.28
	CV (%)	4	17	20	53	53	8	28	11	156	28	262	189
1	C4	2162	71	118	0.28	0.16	3.57	2.74	0.58	98.78	0.23	41	0.47
8		2090	57	144	0.48	0.84	4.43	3.36	0.68	6.53	0.21	46	0.29
10		1972	68	125	0.36	0.21	2.82	64.64	0.62	85.70	0.21	106	111
13		2140	63	138	0.41	0.18	4.24	3.28	0.60	6.33	0.22	29	0.30
14		2185	69	150	1.25	0.56	4.77	4.59	0.65	43.27	0.55	98	0.48
21		2081	69	106	0.49	0.34	4.06	3.55	0.64	7.69	0.24	655	0.35
25		2200	65	100	0.88	0.41	4.05	3.67	0.61	9.99	0.42	37	0.41
	Mean	2119	66	126	0.59	0.38	3.99	12	0.63	37	0.30	145	16
	CV (%)	4	7	15	59	64	16	189	5	109	45	157	258
3	C5	2713	40	157	0.62	0.26	5.67	4.41	0.73	7.21	0.31	34	0.40
9		1944	94	129	0.96	0.50	4.26	3.73	0.64	1347.5	0.40	50	0.45
	Mean	2329	67	143	0.79	0.38	4.97	4.07	0.68	677.35	0.36	42	0.43
	CV (%)	23	56	14	31	45	20	12	9	140	17	27	8
	S.A.	1017	55	45	0.21	0.07	1.73	1.29	0.31	3.40	0.12	28	0.33

CV coefficient of variation, SA source area

Table 6 Results of one-way ANOVA and post-hoc multiple comparison (Tukey test)

Elements	F	<i>p</i>	SSC
Al	36.61	<0.0005	C1 < C3,C4,C5 C2 < C3,C4,C5 C3 < C4,C5
Mn	0.66	0.62	—
Ti	13.57	<0.0005	C1 < C2,C3,C4,C5 C2 < C4,C5 C3 < C4,C5
Sn	0.71	0.59	—
Sb	0.37	0.83	—
V	6.63	0.001	C1,C2,C3 < C5
Cr	0.73	0.58	—
Co	5.91	0.002	C1 < C4,C5 C2 < C4,C5
Cu	5.92	0.002	C1,C2,C3,C4 < C5
Mo	0.97	0.44	—
Zn	0.42	0.79	—
As	0.67	0.62	—

SSC statistically significant comparisons, C cluster

Our analysis of wind frequency and direction measured at site 13, the spatial distribution of element concentrations in lichen transplants and the detection of a local control group provided additional evidence of an association between the biomass power plant and environmental enrichment in Ti, Co, Al, and V. Although the most frequent wind directions (NW and SW) recorded in the study area (Table 4) are consistent with the dominant winds at the regional scale (Atlante Eolico dell'Italia 2015; Troen and Lundtang Petersen 1989), the wind also blew from other directions with an appreciable frequency at all four sites with meteorological stations. Of particular interest for this study, the air flows from SE detected in proximity to the industrial area (site 13) showed a frequency (30 %) about double the average of the other sites (16 %). The meteorological station set up very close to Rende, i.e., S of the power plant, showed that the town is affected by winds blowing from WSW. These winds are attracted by the formation of low-pressure air masses in the urban area, which behaves like a “heat island” (Arnfield 2003), and are directed northward due to the south-north orientation of Rende. Moreover, despite the constantly highest wind velocities recorded at site 13 (Fig. 3), their absolute values are quite low; in fact, the strongest ones can be classified as gentle breezes at most (Scott 2007). This exacerbates the air contamination processes because these winds, far from removing pollutants, promote their slow diffusion in the area surrounding local sources.

When the element concentrations of clusters that emerged from multivariate analyses (NMS and MRPP) are examined, the values of Sn, Cr, Cu, Mo, As, and Zn in cluster C1 can be regarded as low with respect to the environmental quality standards, scales of naturality/contamination (Bargagli and Nimis 2002; Rhoades 1999; Corapi 2011), and the other clusters, whereas those of Al, Ti, Mn, Sb, V, and Co indicate slight enrichment at most. Therefore, we consider this cluster (C1) more suitable than the thalli source area to detect contamination phenomena in the exposure area.

When lichens are transplanted in a new area, they experience an adaptation phase that affects their bioaccumulation capacity (Wolterbeek et al. 2002; Weissman et al. 2005). Moreover, all the lichens in the study area are exposed to the same geological and climatic conditions, so that the lowest concentrations detected in transplanted thalli in a cluster of exposure sites, if comparable with concentrations detected in thalli in uncontaminated areas (on the basis of literature data), can be considered representative of local background concentrations. These values can be used as adequate “blanks” to detect even slight-moderate contamination processes. This hardly can be achieved by means of thalli in the source area, because its internal variability does not give any information about the background variability of the exposure area a value that may be better represented by between sites-variability of an outer control group of stations. We consider this cluster of sites in the exposure area a “local—internal—control group” (Gallo et al. 2014). Due to the lack of confounding factors (Hurlebert 1984) affecting the source area as well as the outer control group of sites, i.e., different meso-climate, local geology, and physiological status of lichens, it provides a better evaluation of the variation of element concentrations in transplanted thalli associated with the main local anthropogenic sources of atmospheric contamination.

The ANOVA results revealed that the only elements showing significant differences between cluster C1 (local control) and the other clusters were (besides Cu) Ti, Co, Al, and V. The highest concentrations of these elements were found at sites of clusters C4 and C5, located mostly leeward (NW and NE sides) of the biomass power plant. The elements with the highest number of comparisons with the internal control showing a significant difference were Ti and Al, whose concentrations in clusters C4 and C5 were comparable to those detected in lichens exposed in urban/industrial areas (Addison and Puckett 1980; Adamo et al. 2003). Seven of the eight sites of cluster C2 (the second lowest mean concentrations) are located windward (S side of the study area) of the power plant, whereas sites of cluster C3 (with intermediate concentrations of Ti and Al) are equally distributed between the S and N sides of the study area. The interspersed position of the sites belonging to different

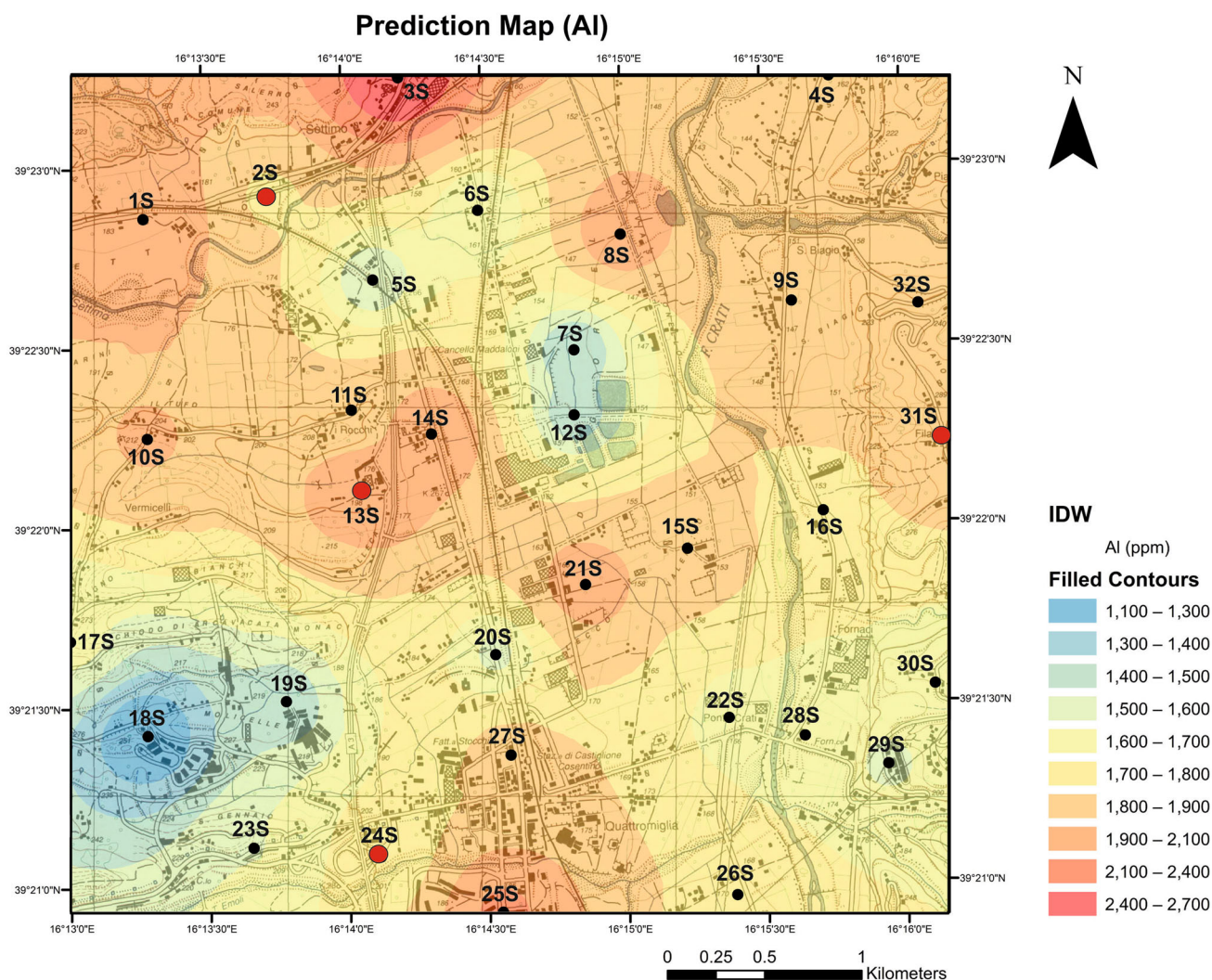


Fig. 5 Contour map showing the spatial distribution of aluminum concentrations measured in thalli of *P. furfuracea* transplanted at the 32 exposure sites

clusters is an expected result. In fact, the interaction between local topography and climate may result in alternating processes of dispersion and deposition of atmospheric pollutants (Koch et al. 1977), generating a patchy distribution of sites with similar near ground concentrations of the same element (Cora and Hung 2003). Sites of clusters C2 and C3 are significantly different from those of clusters C4 and C5. However, for Ti, unlike Al, the mean concentration of cluster C1 is lower than that of C2 ($p < 0.05$), which in turn does not differ from C3 ($p < 0.05$), suggesting that Ti shows more intense (i.e., continuous) contamination than Al. The spatial dispersion of strong, and above all steady, emissions strictly depends on the different frequencies of local wind directions, so that air flows from NW and NE (ca. 30 % of measurements) can result in a lower but still detectable contamination in the S side of the study area (i.e., Ti). Emissions with lower frequency are mostly affected by dominant local winds, so

that contamination is detectable only in the N side (affected by winds blowing from SE and SW) (i.e., Al). This can explain the lack of correlation between PNTWRS and Al concentrations in thalli, because its intense but less frequent emissions from the power plant weaken its association with the frequency of all winds passing through the biomass power plant.

Cobalt and especially vanadium showed a lower number of comparisons with cluster C1 that resulted in a significant difference. Moreover, the association of Co with PNTWRS is probably due to its constant but relatively weak emissions from the power plant, so that it was enriched only in sites leeward (dominant winds) of the biomass power plant (Table 6). As far as Cu is concerned, the significant difference between C5 and all the other clusters is probably due to an outlier in C5 (consisting of just two sites); hence it would be imprudent to seek a cause of this result.

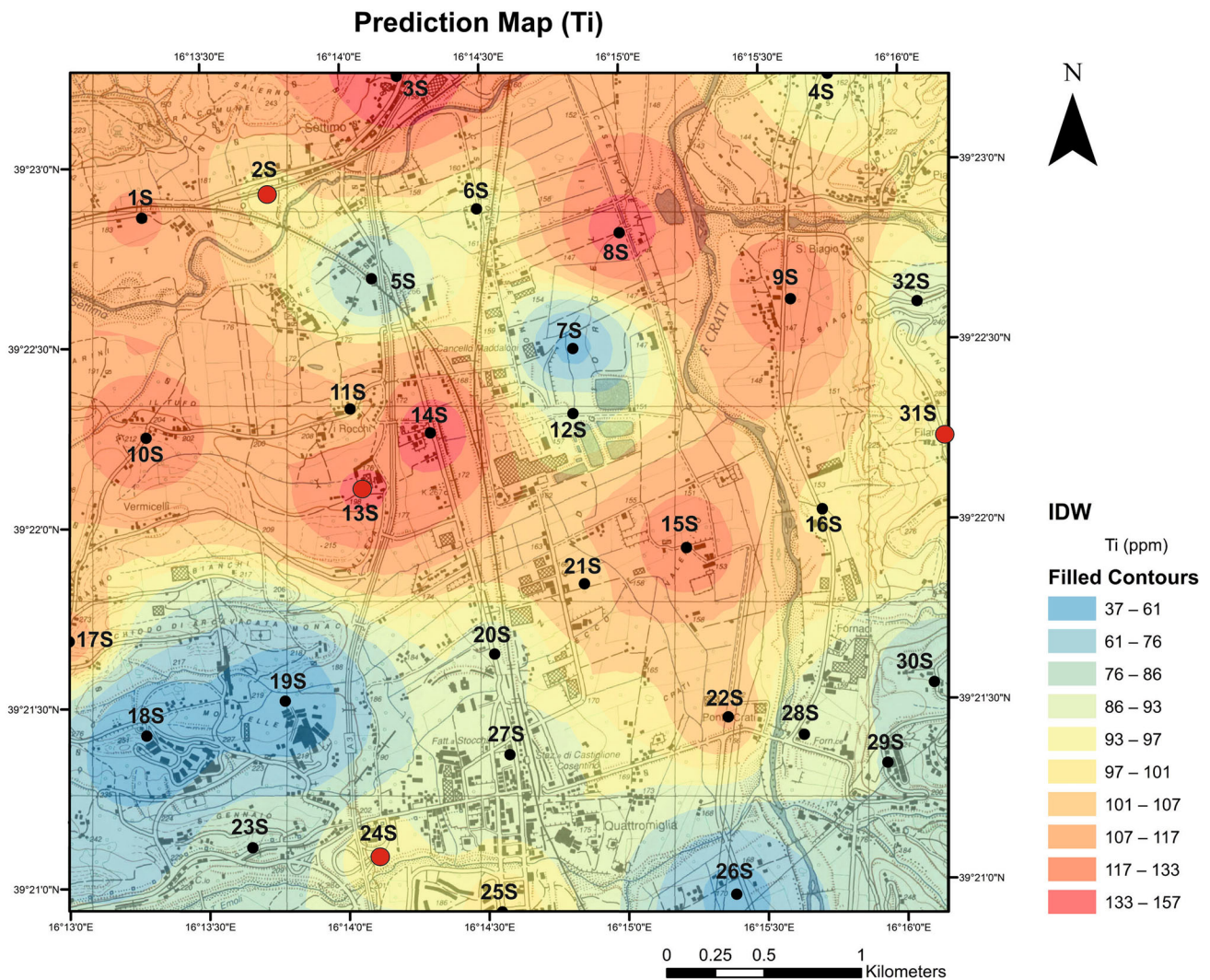


Fig. 6 Contour map showing the spatial distribution of titanium concentrations measured in thalli of *P. furfuracea* transplanted at the 32 exposure sites

Manganese, like Ti and Al, showed a diffuse moderate contamination but unlike these two elements did not covariate with PNTWRS or the concentration ranks of other elements nor did it differ significantly from the local control group. Hence, we can argue that all the local anthropogenic sources of elements significantly contribute to the atmospheric enrichment of Mn. Biomass power plants show high emission factors of Mn (Goovaerts et al. 2001; Sippula et al. 2007) and vehicular traffic releases Mn into the atmosphere in the form of particulate originating from mechanical consumption and tailpipe exhaust, because Mn is a component of a very frequently used anti-knock compound (Egyed and Wood 1996). It is possible that this dual vehicular source of Mn weakens the correlation of this element with Sn, Sb, and Mo, because Mn could be emitted more along expressways than in urban areas with slow traffic flows, as in Rende.

The As, Cr, Cu, and Zn concentrations did not contribute significantly to the atmospheric load at most of the sites, but all of these elements showed scattered high or extremely high values at some exposure sites evenly distributed in the four geographical sides of the study area. These elements show very different traffic emission factors (e.f.) with As (lowest e.f.) differing from Zn (highest e.f.) by ca. 200-fold. Moreover, Zn, Cr, and Cu are mainly associated with tire and brake wear (Schauer et al. 2006), although in the present study they were not significantly correlated with traffic intensity and only mildly correlated with Sb, Sn, and Mo, suggesting that vehicular traffic should not be considered an important contributor to their atmospheric levels. The biomass power plant is fueled by wood manufacturing wastes, wood from thinning of the Sila forests and expired olive pomace (Actelios—Gruppo Falck 2003). Some types of biomass, especially spruce and

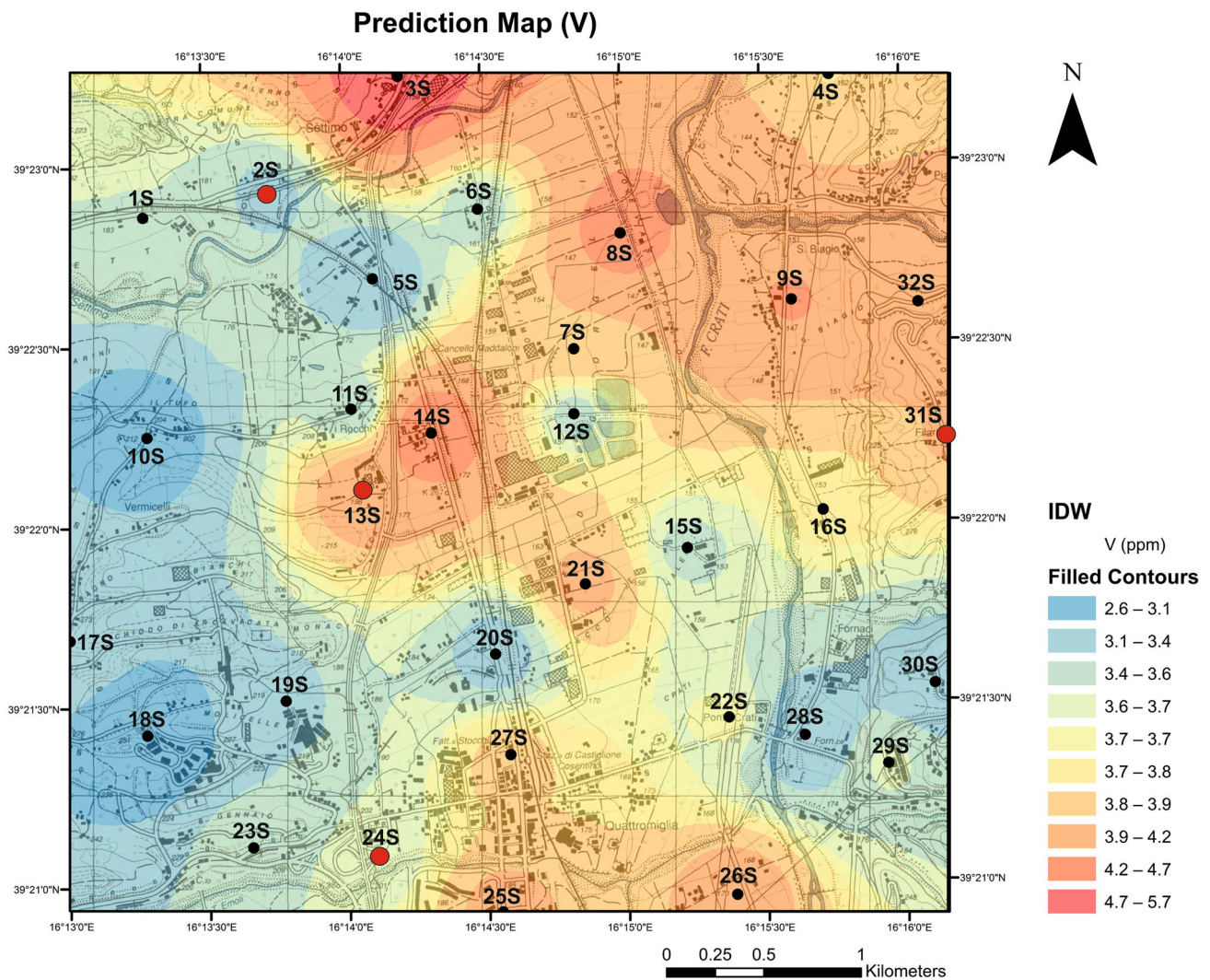


Fig. 7 Contour map showing the spatial distribution of vanadium concentrations measured in thalli of *P. furfuracea* transplanted at the 32 exposure sites

beechwood, can contain high levels of As, Cu, Cr, and Zn (Demirbas 2005; Sippula et al. 2007), and these tree species are well represented within the Sila forests (Pignatti 2011). Italian legislation (D.lgs. 152/2006), according to the Waste Framework Directive (2000), includes chemically treated wood wastes among wood manufacturing wastes; moreover, some types of chemically treated wood can be disposed of by combustion (D.M. February 5, 1998; D.M. n. 186 April 5, 2006) in biomass power plants generating electrical power > 6 MW and one of the most common wood preservatives is copper chromium arsenate (CCA). Thus, when such types of materials are burned, they result in strong atmospheric contamination due to the release of As, Cr, and Cu (Booth 2012; Wasson et al. 2005). Our interpretation of the apparently stochastic spatial distribution of the peaks of these elements is that the biomass power plant episodically burns high quantities of

wood naturally containing and/or chemically enriched in As, Cu, Cr, and Zn, so that the directions of contamination trajectories no longer match the frequency distribution of the local winds.

Conclusions

The results of our study strongly suggest that an effective evaluation of local wind conditions (especially directions and velocities), the calculation of adequate parameters, such as wind frequency, and the time (minutes) needed for winds to travel the distance from the power plant to exposure sites, as well as a monitoring plan based on a sampling design with a high density of exposure sites can be successful in detecting an association between main local anthropogenic sources of elements and their

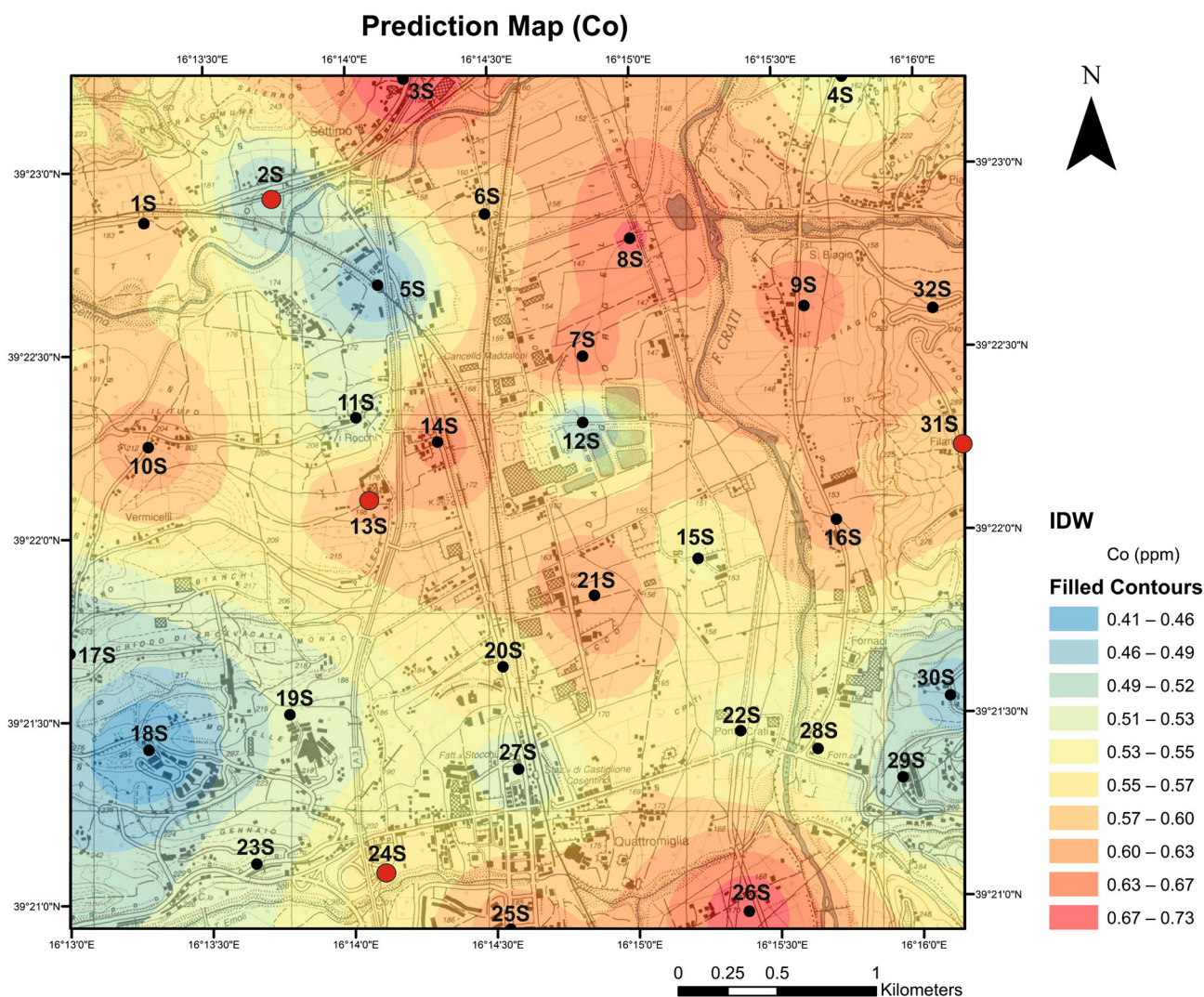


Fig. 8 Contour map showing the spatial distribution of cobalt concentrations measured in thalli of *P. furfuracea* transplanted at the 32 exposure sites

atmospheric enrichment. A univariate-multivariate statistical approach to the element concentrations versus exposure sites dataset made it possible to detect clusters of sites with a different degree of element concentrations and a “local control” group. Matched with wind frequencies evaluated next to the biomass power plant, they were used to determine spatial trends of trace element atmospheric contamination and further supported the association between element enrichment in exposed thalli and the power plant. Among the elements whose spatial variation is associated with the biomass power plant, Ti and Al are those emitted with the highest intensity, although the latter probably with a lower frequency than the former. V and Co emissions are less intense, but the latter is much more frequently emitted than the former. Sb, Sn, and Mo are effective tracers of car exhaust emissions. The explanation of the spatial variation of As, Cr, Cu, and Zn

concentrations is based on the nature of the materials used as fuel in the biomass power plant.

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